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# Diphosphametacyclophanes: Structural and Electronic influences of substituent variation within a family of bis(diketophosphanyl) macrocycles.

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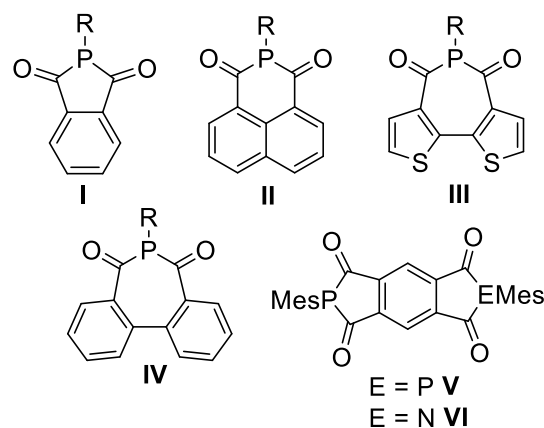
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**ABSTRACT:** The condensation of  $\text{MeP}(\text{SiMe}_3)_2$  with a series of 5-substituted isophthaloyl chlorides ( $5\text{-R}'\text{C}_6\text{H}_3\text{-2,6-}\{\text{C}(\text{O})\text{Cl}\}_2$ ) affords the diphosphametacyclophanes  $m\text{-}\{\text{-C}(\text{O})\text{-C}_6\text{H}_3\text{-5-R}'\text{-C}(\text{O})\text{PMe}\}_2$  ( $\text{R}' = \text{I, Me, 'Bu, Ph, } p\text{-NCC}_6\text{H}_4$ ); the analogues  $m\text{-}\{\text{-C}(\text{O})\text{-C}_5\text{H}_3\text{N-C}(\text{O})\text{PMe}\}_2$  and  $m\text{-}\{\text{-C}(\text{O})\text{-C}_6\text{H}_4\text{-C}(\text{O})\text{PPh}\}_2$  are similarly obtained in preference to higher oligomers, in contrast to precedent reports. The cyclophanes all adopt 'butterfly'-like conformations in the solid state with the P-organyl substituents adopting mutually *exo* arrangements. Structural and computational data suggest the nature of the 5-R substituent is key in directing the inter-ring angle and the extent of LUMO stabilization about the diketophosphanyl scaffold. The latter is substantiated by UV/Vis spectroscopy and cyclic voltammetry, which demonstrate these cyclophanes to be appreciably comparable to the diketophosphanyl systems commonly explored in the context of organic electronic materials; intriguingly, the distinct dikeophosphanyl moieties within the macrocycles appear effectively 'insulated' by the macrocycle geometry, rather than acting as a through-conjugate.

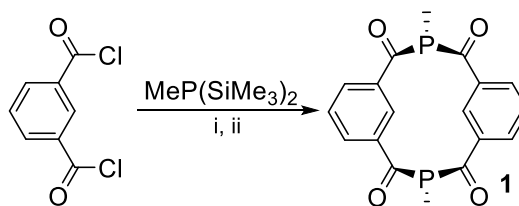
## INTRODUCTION

Organophosphorus compounds have long held ubiquity at the forefront of research across the chemical sciences,<sup>1</sup> their varied applications including, *inter alia*, as synthetic reagents, as ligands stabilizing coordination/organometallic compounds, as a source of asymmetry in catalysis<sup>2</sup> and for their biological activity in agrochemicals and pharmaceuticals.<sup>3</sup> More recent work has focused on the use of phosphanes as components of FLPs to facilitate small molecule activation and in metal-free catalysis.<sup>4</sup> Presently coming to prominence are organophosphanes incorporating  $\alpha$ -acyl moieties, which are finding utility as photoinitiators for polymerization,<sup>5</sup> and more expansively in the broader field of  $\pi$ -conjugated organophosphorus compounds. While  $\pi$ -conjugated materials more generally have been long studied for their potential conductive and photo-absorptive/emissive properties, interest in the incorporation of phosphorus has seen a recent resurgence, with emphasis on developing photosensors and molecular electronic components (e.g. OLEDs, OPVs, MOSFET), in which they assume the acceptor role.<sup>6</sup> This latter application in particular has spawned significant interest in phosphanes featuring two  $\alpha$ -acyl substituents, the so-called diketophosphanyl moiety, viz.  $\text{-C}(\text{O})\text{P}(\text{R})\text{C}(\text{O})\text{-}$ , a component known widely to lower LUMO energies;<sup>7</sup> thus, a growing range of macrocycles featuring this functionality have been reported, typically exploiting an aromatic backbone (Chart 1).<sup>8</sup> Relevant to this activity was our report of the first diphosphametacyclophane,  $\{\text{-C}(\text{O})\text{C}_6\text{H}_4\text{C}(\text{O})\text{P}(\text{Me})\}_2$  (**1**, Scheme 1), which incorporates two diketophosphanyl moieties and arises by self-assembly during the low-temperature condensation of isophthaloyl chloride and  $\text{MeP}(\text{SiMe}_3)_2$ .<sup>9</sup> This remains the only example of this motif and is thus far unexplored in this context.

Chart 1: Representative diketophosphanyl scaffolds<sup>7,8</sup>



Scheme 1. Synthesis of diphosphametacyclophane **1**.



Reagents conditions: i)  $\text{Et}_2\text{O}$ ,  $-78^\circ\text{C}$ ; ii)  $-78^\circ\text{C} \rightarrow \text{r.t.}$ , 12 h.

Cyclophanes in general are a well-established class of macrocycle with numerous applications, including in molecular recognition and host-guest chemistry,<sup>10</sup> selective asymmetric synthesis and catalysis,<sup>11</sup> biomimetics,<sup>12</sup> and more recently molecular electronics.<sup>13</sup> Within many of these roles the incor-

poration of donor atoms is desirable, whether as appended functionalities (e.g. exocyclic phosphanes, phosphates, amines)<sup>14</sup> or as bridging units within the macrocyclic core, such as in the poly(thia)- and poly(aza)-cyclophanes.<sup>15</sup> Synthetically, the latter typically require prolonged, multi-step and/or aggressive protocols, to which one might reasonably attribute the essential neglect of analogues incorporating endocyclic phosphorus moieties. Indeed, this is otherwise remarkable given the enduring impetus for exploring P/N and P/C analogies, and indeed the prevalence of other phosphorus heterocycles that often incorporate an aromatic unit as part of the cyclic skeleton.<sup>16</sup> As such, the isolation of **1** was a significant advance, and its ease of synthesis should offer facile access to an extended range of analogues. Nonetheless, independent efforts to extend this chemistry were seemingly fruitless, Balakrishna *et al* describing a modified protocol for the reaction between 2,6-pyridinedicarbonyl dichloride and phenylphosphane (in the presence of NEt<sub>3</sub>), which affords instead tri- and tetrameric products, the formation of which was tentatively attributed to the ability of the P-aryl substituents to engage in CH- $\pi$  and  $\pi$ - $\pi$  interactions (*cf.* the P-methyls), thus enhancing their stability over the dimeric system.<sup>17</sup>

We have now revisited our synthesis of **1** with a view to both establishing the generality of the synthetic scheme and molecular motif and exploring the electronic features of this class of material, as relevant to opto-electronic materials applications. We thus describe herein an extended range of diphosphametacyclophanes featuring variation of substituents in the aryl 5-position (I, Me, <sup>t</sup>Bu, Ph, C<sub>6</sub>H<sub>4</sub>CN), alongside a pyridyl derivative and indeed the P-phenyl analogue of **1**. We

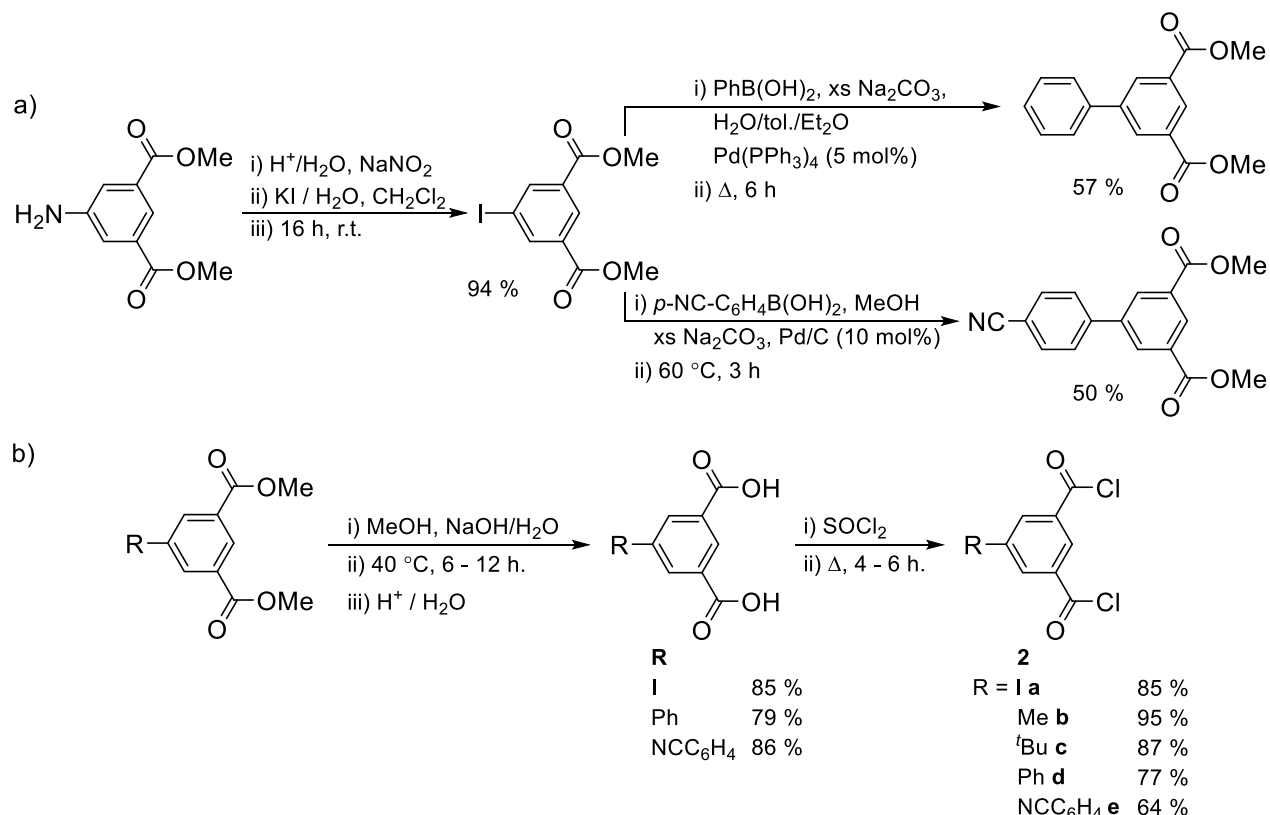
additionally describe structural, electronic, UV-spectroscopic and cyclic voltammetric studies of these macrocycles, providing a baseline assessment of their properties to facilitate development in the context of application.

## RESULTS AND DISCUSSION

There is established precedent for the synthesis of  $\alpha$ -acylphosphanes by condensation of acid chlorides and either primary/secondary phosphanes<sup>18</sup> or related silylphosphanes (RP(SiMe<sub>3</sub>)<sub>2</sub>). In the latter respect, the resulting P-silyl-acylphosphanes (R(Me<sub>3</sub>Si)PC(O)R') typically exhibit only transient stability, undergoing either silatropic rearrangement to afford phosphaaalkenes of the type RP=C(OSiMe<sub>3</sub>)R',<sup>19</sup> or a second condensation to afford bis(acyl)phosphanes. The latter is typical of aryl-1,2-diacid dichlorides, peri-substituted naphthyl derivatives (and related systems, e.g. Chart 1<sup>7,8</sup>) and indeed more flexible long-chain diacid chlorides.<sup>20</sup> In this context, the formation of **1** from isophthaloyl chloride might reasonably be attributed to both the geometric (1,3) disposition of the acyl moieties – precluding the formation of intramolecular macrocycles – and the low steric profile of the P-Me unit providing inadequate kinetic stabilization of the phosphaaalkene. This synthetic route should thus be widely applicable to comparable substrates featuring substitution within the aryl backbone, and perhaps less extensively at the phosphorus center.

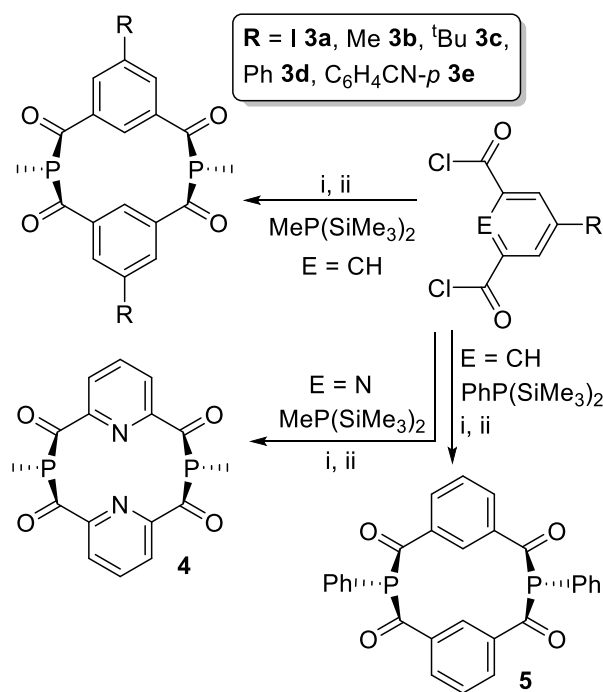
In order to test this hypothesis the 5-substituted isophthaloyl chlorides **2a-e** were each prepared, either directly from literature precedent or via modifications thereof (Scheme 2).<sup>21</sup>

**Scheme 2. Synthesis of 5-R-isophthaloyl derivatives.**



Synthesis of (a) 5-aryl-isophthaloyl esters; (b) 5-R-isophthaloyl chlorides by modifications of literature procedures for R = I.

### Scheme 3. Synthesis of diphosphametacyclophanes.



Conditions: i)  $\text{Et}_2\text{O}$ ,  $-78^\circ\text{C}$ , 30 min, ii)  $-78^\circ\text{C} \rightarrow \text{r.t.}$ , 16 h.

Ethereal solutions of **2a-e** added to stoichiometric  $\text{MeP}(\text{SiMe}_3)_2$  in pre-cooled ( $-78^\circ\text{C}$ ) ether, result in instantaneous color change; thereafter, while attaining ambient temperature over the course of several hours, the respective cyclophanes precipitate from solution (Scheme 3). The crude materials are isolated by filtration and washed (ether) and/or recrystallized ( $\text{CH}_2\text{Cl}_2$  / pentane) to afford pure **3a-e** in low to moderate isolated yield.<sup>22</sup> A comparable approach using pyridine-2,6-dicarbonyl dichloride affords the related cyclophane **4**.

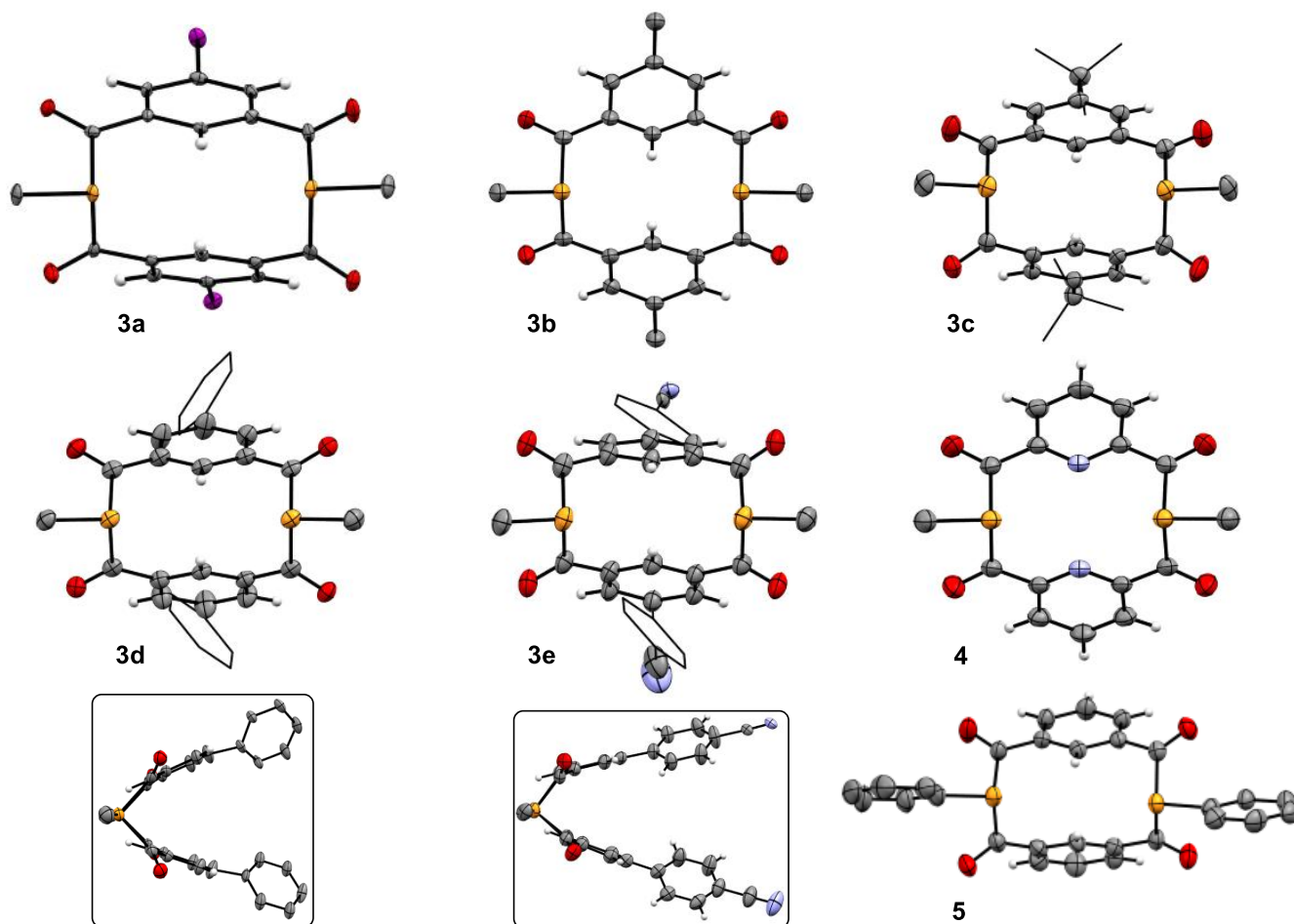
Spectroscopically the cyclophanes appear deceptively simple, their most notable feature being a single resonance in the  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum in the region 30 – 36 ppm (cf.  $\text{MeP}(\text{SiMe}_3)_2$   $\delta_{\text{P}} -196$ ). The associated phosphanyl substituents are apparent in the  $^1\text{H}$ -NMR spectra, their resonances being marginally displaced relative to the parent phosphanes and integrating consistently against those of the aromatic moiety to confirm the 1:1 addition products, while signals associated with the silyl moieties are notably absent. This is reflected by the  $^{13}\text{C}\{^1\text{H}\}$ -NMR data, which further illustrate the high symmetry of the systems and confirm retention of the carbonyl moieties, the stretching modes for which are observed in the infrared spectra. Though none of these data can confirm the dimeric nature of the cyclophanes, the recorded  $^{31}\text{P}$  chemical shifts are consistent with that of **1**, while lying at least 6 – 10 ppm higher than those reported for Balakrishna's trimer and tetramer ( $\delta_{\text{P}} \sim 23$ ),<sup>17</sup> and may thus serve some diagnostic role. Further support for the dimeric nature of the cyclophanes is derived from the observation of associated molecular ions in the mass spectra, and most convincingly from single crystal X-ray diffraction studies across the full series of compounds. The molecular structures are illustrated in Figure 1, with selected geometric parameters summarized in Table 1.

It is noteworthy that we were also able to obtain the P-phenyl analogue **5** in similar fashion from isophthaloyl chlo-

ride and  $\text{PhP}(\text{SiMe}_3)_2$ . Though the isolated yield was extremely low (17 %) data for the crude product demonstrate **5** to be the only phosphorus-containing species, accounting for over 70 % of the mixture, alongside several trace impurities. The removal of the latter incurs appreciable losses due to their comparable solubilities. The  $^{31}\text{P}\{^1\text{H}\}$  NMR signature of **5** ( $\delta_{\text{P}} 30.5$ , cf.  $\text{PhP}(\text{SiMe}_3)_2$   $\delta_{\text{P}} -137$ ) seems consistent with a dimeric motif, as ultimately confirmed by single-crystal X-ray diffraction and HRMS data, albeit that both  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra appear poorly resolved, apparently implicit of dynamic behavior, which we have not been able to identify or preclude.<sup>23</sup> We can nonetheless have confidence in **5** adopting a dimeric structure, in contrast to the tri- or tetrameric motif, as might be anticipated on the basis of Balakrishna *et al.*'s DFT studies. These concluded that P-phenyl derivatives held a general thermodynamic preference for tri- and/or tetramers over the simple diphosphametacyclophanes,<sup>17</sup> with **5** specifically being computed to be 5.3 kcal mol<sup>-1</sup> less favorable than the respective tetracycle, albeit lying slightly lower in energy (0.9 kcal mol<sup>-1</sup>) than the trimer.

Though we have not undertaken a mechanistic study, it is notable that we have not been able to prepare the P-phenyl analogue of **4** from  $\text{PhP}(\text{SiMe}_3)_2$ , nor indeed via Balakrishna's route from  $\text{PhPH}_2$ , which has been unsuccessful in our hands. These reactions instead afforded intractable mixtures, though reaction extracts exhibit data that might imply formation of transient phosphalkenes, the polymerization of which is thus likely. We have also obtained comparable results in attempts to prepare P-Bu and P-Mes analogues of **3** and **4**, suggesting a delicate balance between the double-condensation and silatropic rearrangement pathways. It thus seems likely that the formation of dimers vs trimers / tetramers will be similarly influenced by kinetic factors, and thus reaction protocol, over pure thermodynamic arguments.

**Structural and electronic properties.** Structurally, each of **3a-e**, **4** and **5** adopts a 'butterfly' conformation, comparable to that previously described for **1** and precedent diaza[3.3]metacyclophanes.<sup>24</sup> This is enforced by the pseudopyramidal phosphorus centers, the substituents of which adopt a mutually *exo* arrangement, while the skeletal aromatic rings are appreciably displaced from coplanarity. The extent of this displacement varies across the series, being most pronounced for **4**, in which the rings are close to orthogonal ( $\angle 86.23^\circ$ ), and least in the case of **3e** ( $\angle 34.25^\circ$ ). Indeed, the nature of the aromatic unit would seem influential in this respect, the displacement becoming less pronounced with increasingly positive Hammett ( $\sigma_{\text{m}}$ ) parameters for the 5-R substituent; both **1** and **5** are broadly in the middle of the series and exhibit notably little variation derived from the nature of the P-organyl. These trends are broadly replicated by DFT studies at the B3LYP/6-311G(3d,3p) level, albeit that computed displacement angles deviate from experiment, suggestive of packing effects in the solid state. Indeed, this is clearly illustrated in the case of **3b** for which the computed gas-phase displacement ( $\angle 56.37^\circ$ ) is significantly lower than that observed in the crystal ( $\angle 83.84^\circ$ ); the latter appears heavily directed by a network of hydrogen bonding between the 5-Me substituent and the carbonyls of adjacent molecules, augmented by intermolecular methyl C-H... $\pi$  interactions, resulting in a nested array of molecules through the crystal (SI figure S105). A similar packing arrangement is noted for pyridyl

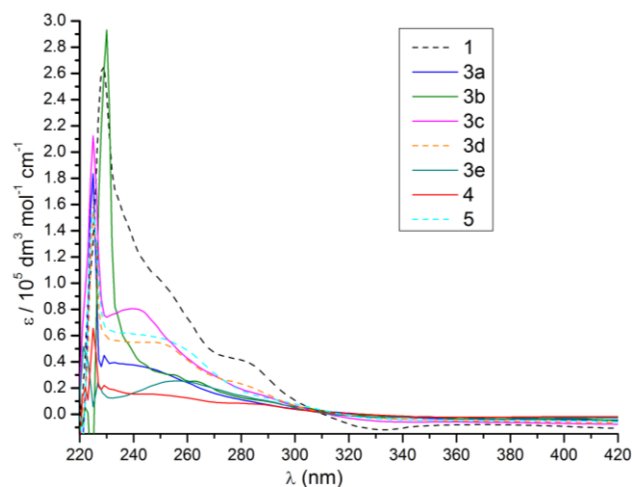


**Figure 1** Molecular structures of **3a-e**, **4** and **5** with displacement ellipsoids at the 50% level, ancillary hydrogen atoms omitted and peripheral functional groups reduced for clarity. Insets illustrate side-on projections of the 5-aryl systems. Selected, comparative, geometric data are summarized in Table 1.

derivative **4**, accounting for the slightly smaller computed displacement ( $\angle 80.89^\circ$ ) relative to experiment; however, the much closer agreement in this case does support the adopted structure being heavily directed by the pyridyl moiety.

Some insight into this conformational preference can be derived from the computational data, which reveal for **1**, **3a-e** and **5** an appreciable inter-ring bonding interaction lying between 1 and 1.3 eV (ca 1.8 eV for **1**) below the HOMO, constraining their proximity and disposition within the macrocyclic core; in contrast, the equivalent interaction within pyridyl derivative **4** (ca 2 eV below the HOMO) is localized to the nitrogen centers, leading to a significant widening of the inter-ring angle. Beyond this feature the orbital distributions are largely comparable across the series, the HOMO being typically dominated by the diketophosphanyl moieties, with significant contribution from the phosphorus lone pairs; this is also reflected in the essentially degenerate HOMO-1, while the aromatic skeleton (and 5-R substituents) features in successively lower energy orbitals. The distribution of the virtual orbitals (up to LUMO+5) is similarly consistent across the series, these being essentially composed of  $\pi^*$  symmetry about the carbonyls and skeletal aromatic moieties, in line with the wider range of diketophosphanyl compounds reported to date. Though no clear trend in energies is apparent, there would seem to be a marginal stabilizing of the LUMO as the 5-R

substituent becomes more electron withdrawing, that of **3a** (R = I) being ca 0.25 eV more stable than in **3c** (R = *t*Bu), which represent the extremes of the series. In contrast, the HOMO

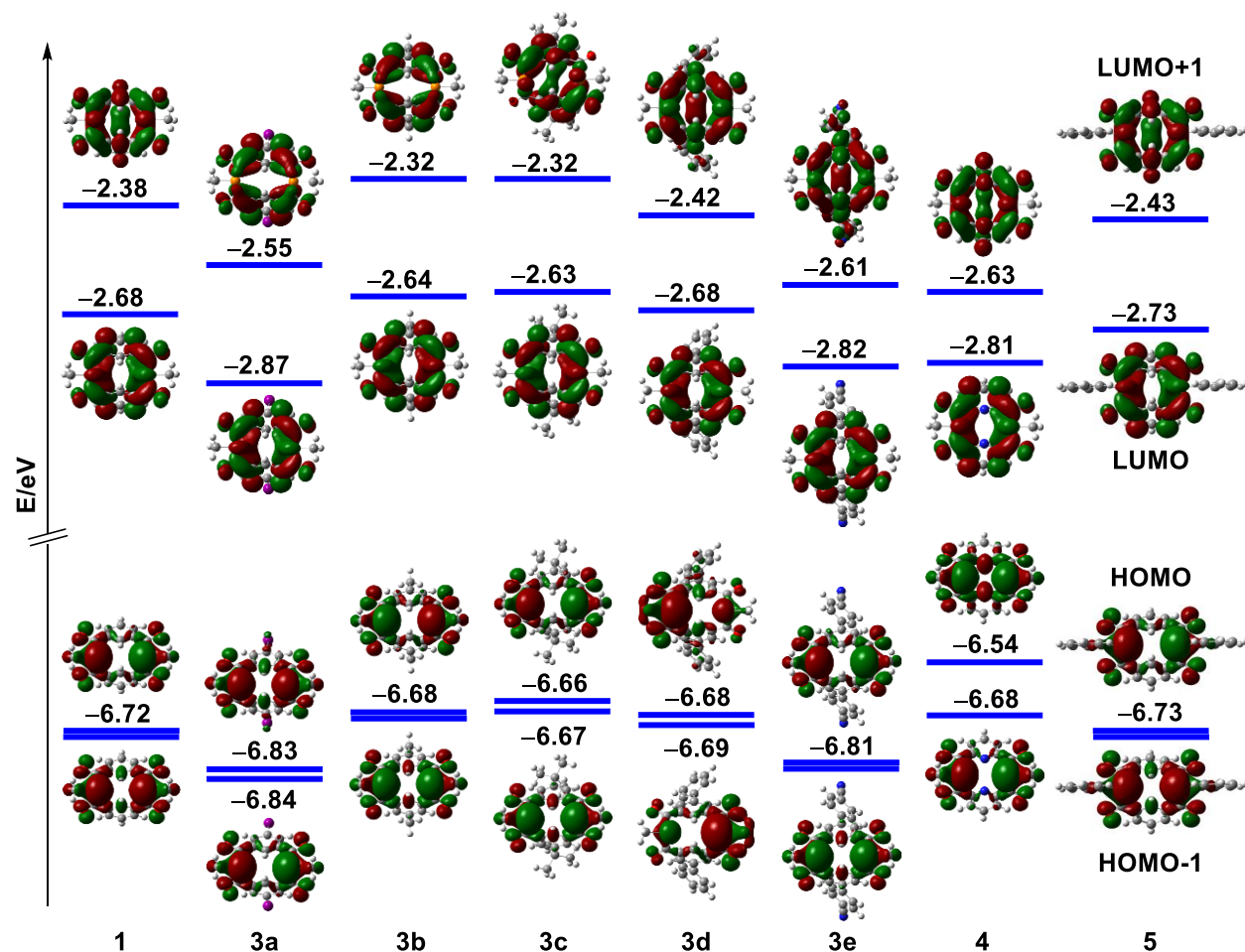


**Figure 3:** UV/vis absorption spectra for **1**, **3a-e**, **4** and **5**, obtained at room temperature as dilute ( $10^{-5}$  M) solutions in  $\text{CH}_2\text{Cl}_2$ .

**Table 1. Selected geometric parameters<sup>a</sup> for 1, 3a-e, 4 and 5**

	1 <sup>b</sup>	3a	3b	3c	3d	3e	4	5 <sup>c</sup>
<b>C–O</b>	1.210(3), 1.202(3), 1.220(3), 1.211(3)	1.197(6), 1.211(6), 1.212(6), 1.207(6)	1.207(4)	1.212(2), 1.206(3), 1.207(2), 1.206(2)	1.214(3), 1.214(2), 1.216(2), 1.212(2)	1.224(6), 1.206(5), 1.206(5), 1.214(6)	1.215(3)	1.198(7), 1.199(5), 1.203(6), 1.200(7)
<b>P–C<sub>CO</sub></b>	1.892(3), 1.890(3), 1.894(3), 1.886(3)	1.898(5), 1.891(4), 1.887(5), 1.899(5)	1.909(3)	1.892(2), 1.884(2), 1.900(2), 1.882(2)	1.890(2), 1.890(2), 1.892(2), 1.886(2)	1.882(4), 1.895(5), 1.889(4), 1.880(5)	1.892(2)	1.893(5), 1.908(5), 1.894(5), 1.888(5)
<b>P–C<sub>R</sub></b>	1.814(4), 1.816(4)	1.810(5), 1.822(5)	1.825(4)	1.819(2), 1.819(2)	1.821(2), 1.817(2)	1.821(6), 1.818(5)	1.834(4)	1.816(4), 1.824(4)
<b>C<sub>CO</sub>–C<sub>Ar</sub></b>	1.492(4), 1.494(4), 1.495(4), 1.494(4)	1.496(6), 1.490(7), 1.491(6), 1.495(6)	1.487(4)	1.484(2), 1.494(2), 1.494(2), 1.491(3)	1.490(3), 1.490(3), 1.493(3), 1.491(3)	1.484(6), 1.503(6), 1.499(6), 1.493(6)	1.491(3)	1.490(6), 1.492(6), 1.486(6), 1.488(6)
<b>C<sub>CO</sub>–P–C<sub>CO</sub></b>	95.73(13), 95.14(12)	92.93(19), 95.1(2)	97.92(15)	94.25(8), 96.02(8)	96.65(9), 93.47(9)	93.45(19), 95.68(19)	97.08(9)	96.9(2), 98.6(2)
<b>P–C–C<sub>Ar</sub></b>	117.54(18), 117.09(18), 117.32(19), 118.22(19)	116.1(3), 118.0(3), 119.0(3), 116.3(3)	119.2(2)	119.23(12), 118.21(13), 116.04(12), 116.04(13)	117.90(14), 117.84(14), 117.83(14), 117.97(14)	118.4(3), 118.1(3), 116.8(3), 115.3(3)	119.80(14)	116.7(3), 116.6(3), 118.0(3), 117.5(3)
<b>∠Ar<sup>d</sup> (expt)<sup>e</sup></b>	41.64	38.81	83.84	45.49	43.88	34.25	86.23	41.54
<b>∠Ar<sup>d</sup> (calc)<sup>f</sup></b>	56.47	57.33	56.37	58.62	53.76	55.96	80.39	54.18

<sup>a</sup>distances in Å, angles in °. <sup>b</sup>as previously reported in ref 12. <sup>c</sup>data for compound 5 confirm connectivity but parameters warrant caution due to incomplete data. <sup>d</sup>inter-ring displacement angle, measure between planes defined by skeletal aromatic rings. <sup>e</sup>calculated from X-ray data using Mercury. <sup>f</sup>geometry optimized at B3LYP/6311G(3d,3p).



**Figure 2.** Calculated frontier orbitals for the diphosphametacyclophanes at the B3LYP/6-311G(3d,3p) level.



**Table 2 Absorption maxima and extinction coefficients for diphosphametacyclophanes.<sup>a</sup>**

	$\lambda_{\text{max}} / \text{nm} [\epsilon / 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}]$				
<b>1</b>	229 [26.52]	250 [10.21]	279 [4.24]	365 [0.64]	415 [0.43]
<b>3a</b>	225 [18.35]	250 [3.25]	283 [0.99]	319 [0.10]	395 [0.37]
<b>3b</b>	230 [29.30]	256 [2.96]	290 [0.96]	303 [0.51]	365 [0.19]
<b>3c</b>	225 [21.24]	240 [8.05]	286 [1.56]	330 [0.27]	370 [0.17]
<b>3d</b>	225 [15.97]	246 [5.49]	280 [2.37]	380 [0.42]	415 [0.31]
<b>3e</b>	221 [5.16]	256 [2.54]	290 [0.99]		
<b>4</b>	225 [6.56]	245 [1.54]	281 [0.82]	322 [0.02]	415 [0.04]
<b>5</b>	225 [15.52]	255 [5.43]	294 [1.05]		

<sup>a</sup>recorded at room temperature for dilute ( $10^{-5}$  M) solutions in  $\text{CH}_2\text{Cl}_2$ .

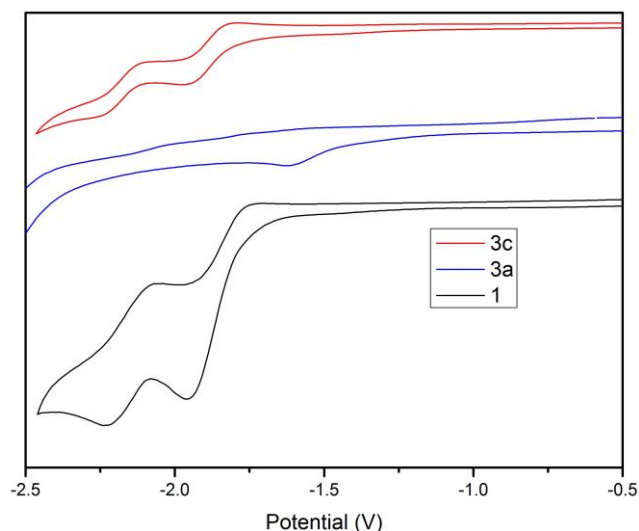
energies – and thus HOMO-LUMO separations – show no such correlation (Figure 2). The electronic similarities across the series are also reflected in the UV-vis spectra (Figure 3, Table 2, see also SI fig S71 – S73), which each exhibit notable absorption maxima around  $\lambda_{\text{max}} = 225, 250$  and  $280$  nm. These data are assigned with the aid of TDDFT calculations that broadly reflect the key features of the spectra (SI, Fig. S74-S91).<sup>25</sup> Thus, the highest energy feature (ca 225 nm), which appears unusually sharp,<sup>26</sup> is each case associated a single, dominant  $\pi_{\text{Ar}} \rightarrow \pi^*_{(\text{CO/Ar})}$  excitation from the HOMO-5 / HOMO-8 levels into low-lying acceptor orbitals (LUMO to LUMO+3). In the case of **3c** and **3d** this is augmented by a smaller contribution from  $n \rightarrow \pi^*_{(\text{CO/Ar})}$  transitions originating in the occupied phosphorus  $p_z$  orbital (HOMO-8  $\rightarrow$  LUMO+2 and HOMO-11  $\rightarrow$  LUMO+1 respectively). This feature is most prominent for **1** and **3b**, for which it is marginally red-shifted (ca 5 nm), while for **3e**, it is both weaker and shifted to higher energy (221 nm); the remaining systems appear largely comparable, albeit that pyridyl derivative **4** exhibits much lower intensity absorption across the full spectrum. The subsequent absorptions in each case are consistently composed of  $\pi \rightarrow \pi^*$  transitions from successively lower-lying occupied orbitals to the LUMO / LUMO+1 levels, augmented by increasing contributions from  $n \rightarrow \pi^*$  between the phosphorus lone-pairs (HOMO / HOMO-1) and higher-lying virtual orbitals (LUMO+3). Additionally, much weaker, broad features are generally apparent around 300-350 nm and 400 nm, albeit not convincingly observed for **3e** or **5**. These absorbances are associated with transitions between the frontier orbitals, *viz.* HOMO  $\rightarrow$  LUMO, HOMO-1  $\rightarrow$  LUMO and HOMO  $\rightarrow$  LUMO+1, and essentially composed of  $n \rightarrow \pi^*$  from the phosphorus lone-pairs to the extended aryl-diketophosphanyl moieties. We note that in contrast to many precedent diketophosphanyl compounds, none of **1**, or **3 – 5** exhibit any fluorescent behaviour. Nonetheless, the features of the absorption spectra are, overall, consistent with that previously described for related compounds, in particular Takeda's superficially related phosphaphthalimides.<sup>8b</sup> Such close comparability seems somewhat surprising, given the presence of a second diketophosphanyl moiety, which one might intuitively expect to further reduce the LUMO energy and thus influence appreciably the absorption maxima; this influence would rather appear negligible.

In order to further probe the electronic nature of these compounds cyclic voltammetry was conducted of  $\text{CH}_2\text{Cl}_2$  solutions at a platinum disk (1 mm) working electrode with  $\text{NBu}_4\text{PF}_6$

**Table 3 Electrochemical data for diphosphametacyclophanes<sup>a</sup>**

	$^1E_{1/2} / \text{V}^c$	$^2E_{1/2} / \text{V}^c$	$E_{\text{LUMO}}^d / \text{eV}$
<b>1</b>	−1.84	−2.15	−2.96
<b>3a</b>	−1.61 <sup>e</sup>	–	−3.19 <sup>f</sup>
<b>3c</b>	−1.89	−2.23	−2.91
<b>3d</b>	−1.73	−2.04	−3.07
<b>3e</b>	−1.74	−2.11	−3.06
<b>4</b>	−1.74	−2.12	−3.06

<sup>a</sup>Cyclic Voltammetry data for 0.1 M analyte solutions in  $\text{CH}_2\text{Cl}_2$ , with 0.1 M  $\text{NBu}_4\text{PF}_6$  supporting electrolyte at  $100 \text{ mV s}^{-1}$ . <sup>b</sup>Voltammetry data for **3b** and **5** were not observed. <sup>c</sup>Half-potentials for first and second (quasi-reversible) reductive events relative to  $\text{Fc}/\text{Fc}^+$  couple. <sup>d</sup>Estimated using  $E_{\text{LUMO}} = -(4.8 + ^1E_{1/2})$ .<sup>27</sup> <sup>e</sup> $E_{\text{pc}}$  for irreversible reduction. <sup>f</sup>Estimated using  $E_{\text{pc}}$ .<sup>28</sup>

**Figure 4.** Representative cyclic voltammograms (relative to  $\text{Fc}/\text{Fc}^+$ ) at scan rates of  $100 \text{ mV s}^{-1}$  (**1**, **3c**) or  $200 \text{ mV s}^{-1}$  (**3a**). See SI (S92-S97) for all plots.

supporting electrolyte. Key data are summarized in Table 3, with illustrative voltammograms in Figure 4. The archetypal **1** and derivatives **3c–e** each exhibit two pseudo-reversible reductions around  $-1.8$  and  $-2.1$  V relative to the  $\text{Fc}/\text{Fc}^+$  couple, as does the pyridyl analogue **4**. In contrast, the 5-iodo derivative **3a** exhibits a single, irreversible, reductive feature around  $-1.6$  V, which is only well resolved at higher scan rates ( $>200 \text{ mV s}^{-1}$ ). The earlier onset of this process would appear in line with the noted stabilization of the LUMO of **3a** (*vide supra*) relative to those with more donating substituents. Indeed, experimental estimates of the LUMO energies<sup>27</sup> support this, suggesting that of **3a** ( $E_{\text{LUMO}} \sim -3.19 \text{ eV}$ )<sup>28</sup> lies ca  $0.15 \text{ eV}$  lower than for most of the series, the closest comparators being the 5-aryl systems **3d** ( $-3.07 \text{ eV}$ ) and **3e** ( $-3.06 \text{ eV}$ ) and pyridyl derivative **4** ( $-3.06 \text{ eV}$ ). The least stabilized LUMO is associated with **3c** (5-*t*Bu;  $-2.91 \text{ eV}$ ), again in line with the computational data.

These data suggest the extent of LUMO stabilization within the cyclophane scaffold is comparable to that of the simpler aromatic diketophosphanyls of types **I** and **II** (Chart 1), which also show similar trends in response to the introduction of substituents on the aromatic backbone. It is notable that the

cyclophanes exhibit no additional stabilization of the LUMO as a result of the second diketophosphanyl moiety, in contrast to the only precedent bis(diketophosphanyl) compound (**V**, Chart 1),<sup>8c</sup> the LUMO of which is appreciably lowered in energy (ca 0.6 eV) relative to **I**<sup>Mes</sup> (Chart 1, R = Mes). This disparity of behavior presumably reflects relatively diminished conjugation within the cyclophanes, as might be inferred (*vide supra*) from the HOMO and HOMO-1, which are dominated by the phosphorus lone pairs, rather than the aromatic cores, as is more commonly observed; this is, in part, presumably a corollary of the meta geometry. The LUMOs, in turn, comprise a nodal plane that bisects both arenes, essentially affording two isolated diketophosphanyl systems, rather than a fully delocalized regime; thus, the system would seem to behave as two discrete molecular fragments.

## CONCLUSIONS

We have reported the synthesis of a family of macrocyclic diphosphanes built around a common meta-cyclophane core, with variation of substituents in the 5-position of the aromatic bridges, alongside an analogue based on a pyridyl backbone. These compounds are readily obtained from the condensation of the disilylphosphane MeP(SiMe<sub>3</sub>)<sub>2</sub> and respective aromatic 1,3-diacid chlorides and are fully characterized, including by X-ray diffraction. Significantly, PhP(SiMe<sub>3</sub>)<sub>2</sub> and isophthaloyl chloride react to afford the P-phenyl analogue **5**, rather than a tri-/tetramer as has been previously predicted. This would suggest simple thermodynamic stability is an inadequate guide as to the outcome of these reactions, which seem governed by subtler kinetic factors.

UV-vis spectroscopic and cyclic voltammetry data, augmented by DFT studies, demonstrate the cyclophanes to be substantially comparable, from an electronic standpoint, to the relatively small range of precedent aromatic diketophosphanyls. Indeed, despite the incorporation of this moiety being typically accepted to afford reduced LUMO energies, the influence of having two within these cyclophanes is negligible. This seemingly reflects a loss of conjugation within the aromatic fragments, which we attribute to the meta-geometry (*cf. ortho*, or *peri*-naphthyl in precedent examples). This is also evident from observation of a nodal plane within the computed LUMOs (*cf.* fully delocalized  $\pi^*$  orbitals in precedent cases) that results in two isolated diketophosphanyl systems. This break in conjugation can presumably be invoked to account for the lack of any fluorescent behavior within these systems, in contrast to many aromatic-based diketophosphanyl scaffolds.

The occupied frontier orbitals of the cyclophanes are also disparate from precedent diketophosphanyls, being heavily localized about the phosphorus lone-pairs, rather than the  $\pi$ -system. This feature would suggest that the cyclophanes might be favorable toward ligation (as indeed we have noted previously<sup>9</sup>). Aside from the obvious intrinsic potential as sterically encumbering ligand, this may also present an opportunity to modify photophysical properties, as has been previously observed for diketophosphanyl derivatives,<sup>8</sup> offering a possible means of accessing the presently absent fluorescent behavior. This is a possibility that we are currently exploring.

## EXPERIMENTAL SECTION

**General Methods.** All manipulations were performed under strict anaerobic conditions using standard Schlenk line and glovebox (MBraun) techniques, working under an atmosphere of dry argon or dinitrogen respectively. Solvents were distilled under nitrogen from potassium (THF, benzene, toluene), sodium-potassium alloy (pentane, hexane, Et<sub>2</sub>O) or CaH<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub>) and stored over molecular sieves (4 Å, for CH<sub>2</sub>Cl<sub>2</sub>, THF, Et<sub>2</sub>O, benzene) or potassium mirrors (pentane, hexane). Deuterated solvents were dried in comparable fashion, freeze-thaw degassed and stored in a glovebox. Isophthaloyl chloride and 2,6-pyridine dicarbonyl dichloride were obtained from Sigma-Aldrich of Fisher and recrystallized prior to use; 5-Methylisophthalic acid and 5-*t*-butyl isophthalic acid were purchased from Sigma-Aldrich and used as received; 5-iodoisophthalic<sup>21b</sup> acid and 3-phenyl isophthalic acid<sup>21f</sup> were prepared by literature methods. The silylphosphanes RP(SiMe<sub>3</sub>)<sub>2</sub> (R = Me, Ph) were prepared as previously described.<sup>20</sup>

NMR spectra were recorded at 303 K, on Varian VNMRS 400 (<sup>1</sup>H 399.50 MHz, <sup>13</sup>C 100.46 MHz, <sup>31</sup>P 161.71 MHz, <sup>29</sup>Si 79.37 MHz) or 600 (<sup>1</sup>H 599.68 MHz, <sup>13</sup>C 150.81 MHz) spectrometers. All spectra are referenced to external Me<sub>4</sub>Si or 85 % H<sub>3</sub>PO<sub>4</sub> as appropriate. Carbon-13 spectra were assigned by recourse to the 2D (HSQC, HMBC) spectra. UV-vis spectra were recorded using either a Perkin Elmer Lambda 265, Varian Carey 50, or Biowave II+ spectrometer (figures generated using the Lambda 265 data); IR spectra were recorded as solids on a Perkin Elmer Spectrum One instrument. Elemental analyses (performed by Mr S. Boyer of the London Metropolitan University Elemental Analysis Service) were obtained on samples taken from the bulk material yielded by the final purification step indicated in the experimental text. Mass spectra were recorded by D A. Abdul-Sada of the departmental service.

**Electrochemistry.** Cyclic voltammograms were obtained under anaerobic conditions (MBraun glovebox under catalytically purified argon) at 298 K, for CH<sub>2</sub>Cl<sub>2</sub> solutions (10<sup>-5</sup> M) with 0.1 M [nBu<sub>4</sub>N]PF<sub>6</sub> supporting electrolyte, using a 3-electrode cell comprising platinum disk working electrode (1 mm), platinum wire counter electrode and silver wire pseudoreference. Data were recorded using a PalmSens Emstat3+ Blue potentiostat and the PSTrace software package. Potentials are reported relative to the Fc/Fc<sup>+</sup> couple of a doped sample.

### Synthesis Hazard Information.

*Silyl-phosphanes are intrinsically pyrophoric and require handling under stringently anaerobic and moisture-free conditions. The cyclophanes should be handled under comparable conditions, being extremely air/moisture sensitive, though we have not noted any pyrophoric tendencies.*

**Synthesis of 5-(4-Cyanophenyl)benzene-1,3-dicarboxylic acid** Dimethyl 4-cyanobiphenyl-3,5-dicarboxylate (1.19 g, 4.01 mmol) was dissolved in MeOH (30 cm<sup>3</sup>), NaOH (0.48 g, 12.09 mmol) in water (10 cm<sup>3</sup>) was added and the mixture was heated to 40 °C for 4 hours via bead bath. After cooling to ambient temperature, the reaction mixture was acidified to ca. pH 7 to afford an off-white precipitate which was dried in a desiccator overnight. Yield: 0.93 g, 86 %. <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>SO, 599.68 MHz):  $\delta_{\text{H}}$  = 13.50 (br, OH, 2H), 8.51 (t, aromatic CH-2, <sup>2</sup>J<sub>HH</sub> = 1.45 Hz, 1H), 8.43 (d, ArH<sup>4/6</sup>, <sup>2</sup>J<sub>HH</sub> = 1.45 Hz, 2H), 7.98 (Ph, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 150.81 MHz):  $\delta_{\text{C}}$  = 166.3 (C=O), 142.9 (CN), 139.4, 133.1, 132.3, 131.7, 129.9, 128.1, 118.7, 110.1. HRMS (ESI) (m/z): Calcd for C<sub>15</sub>H<sub>10</sub>NO<sub>4</sub> 268.0610 ([MH]<sup>+</sup>). Found 268.0617 ([MH]<sup>+</sup>).

**Synthesis of 5-Iodoisophthaloyl chloride (2a)** Thionyl chloride (10 cm<sup>3</sup>) was added to a round-bottom-Schlenk containing 5-iodoisophthalic acid (0.172 g, 0.59 mmol), the flask was fitted with a condenser and refluxed for 4 hours *via* a bead bath, before removing the volatiles under reduced pressure, affording 0.165 g of an orange/red oil, 85 % yield. NMR data agree with the literature.<sup>21c</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 8.79 (br t, ArH<sup>2</sup>, 1H), 8.69 (d, ArH<sup>4/6</sup>, <sup>2</sup>J<sub>HH</sub> = 1.6 Hz, 2H).

**Synthesis of 5-Methylisophthaloyl dichloride (2b)** Following from literature,<sup>21h</sup> 5-Methylisophthalic acid (2 g, 11.1 mmol) in thionyl chloride (10 cm<sup>3</sup>) was refluxed for 6 hours in a bead bath. After



cooling, the volatiles were removed under reduced pressure to afford a pale-yellow solid. Yield: 2.3 g, 95 %.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 599.68 MHz):  $\delta_{\text{H}} = 8.67$  (s,  $\text{ArH}^2$ , 1H), 8.21 (s,  $\text{ArH}^{4/6}$ , 2H), 2.55 (s,  $\text{CH}_3$ , 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 150.81 MHz):  $\delta_{\text{C}} = 167.6$  (s,  $\text{C}=\text{O}$ ), 140.6 (s,  $\text{C}^5$ ) 137.7 (s,  $\text{C}^{4/6}$ ), 134.4 ((s,  $\text{C}^{1/3}$ ), 131.4 (s,  $\text{C}^2$ ), 21.2 (s,  $\text{CH}_3$ ).

**Synthesis of 5-Tertbutylsophthaloyl chloride (2c)** Thionyl chloride (10  $\text{cm}^3$ ) was added to a round-bottom-Schlenk containing 5-tertbutyl isophthalic acid (5 g, 22.5 mmol), the flask was fitted with a condenser and refluxed for 4 hours via a bead bath before removing the volatiles under reduced pressure, affording 5.097 g of colorless solid, 87.4 % yield. The NMR data agree with the literature.<sup>21d</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{H}} = 8.71$  (t,  $\text{ArH}^2$ ,  $^2J_{\text{HH}} = 1.6$  Hz, 1H), 8.41 (d,  $\text{ArH}^{4/6}$ ,  $^2J_{\text{HH}} = 1.6$  Hz, 2H), 1.42 (s,  $\text{C}(\text{CH}_3)_3$ , 9H).

**5-Phenylisophthaloyl chloride (2d)** Following from literature,<sup>21i</sup> 5-Phenylisophthalic acid (2 g, 11.1 mmol) in thionyl chloride (10  $\text{cm}^3$ ) was refluxed for 6 hours in a bead bath. After cooling, the volatiles were removed under reduced pressure to afford a colorless solid. Yield: 0.321 g, 77 %.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 399.49 MHz):  $\delta_{\text{H}} = 8.82$  (br t,  $\text{ArH}^2$ , 1H), 8.6 (d,  $\text{ArH}^{4/6}$ ,  $^1J_{\text{HH}} = 1.5$  Hz, 2H), 7.65 (d,  $\text{ArH}^{8/12}$ ,  $^1J_{\text{HH}} = 7.32$  Hz, 2H), 7.56-7.42 (m,  $\text{ArH}^{9/11} + \text{ArH}^{10}$  (overlapped), 3H).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 599.68 MHz):  $\delta_{\text{H}} = 8.82$  (br t,  $\text{ArH}^2$ , 1H), 8.6 (dd,  $\text{ArH}^{4/6}$ ,  $^1J_{\text{HH}} = 1.6$  Hz, 2H), 7.65 (d,  $\text{ArH}^{8/12}$ ,  $^1J_{\text{HH}} = 7.31$  Hz, 2H), 7.54 (t,  $\text{ArH}^{9/11}$ ,  $^1J_{\text{HH}} = 7.31$  Hz, 2H), 7.49 (t,  $\text{ArH}^{10}$ , 7.31 Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 150.81 MHz):  $\delta_{\text{C}} = 167.6$  (s,  $\text{C}=\text{O}$ ), 143.8 (s,  $\text{C}^5$ ), 137.6 (s,  $\text{C}^7$ ), 135.5 (s,  $\text{C}^{4/6}$ ), 135.1 (s,  $\text{C}^{10}$ ), 132.4 (s,  $\text{C}^{1/3}$ ), 129.6 (s,  $\text{C}^{8/12}$ ), 129.4 (s,  $\text{C}^2$ ), 127.4 (s,  $\text{C}^{9/11}$ ).

**Cyanobiphenyl diacyl chloride (2e)** 5-Cyanophenylisophthalic acid (0.6 g, 2.2 mmol) in thionyl chloride (20  $\text{cm}^3$ ) was refluxed for 6 hours in a bead bath. After cooling, the volatiles were removed under reduced pressure to afford an off-white/pale-orange solid. Yield: 0.43 g, 64 %.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{H}} = 8.90$  (br t,  $\text{ArH}^2$ , 1H), 8.59 (d,  $\text{ArH}^{4/6}$ ,  $^2J_{\text{HH}} = 1.5$  Hz, 2H), 7.85 (d,  $\text{ArH}^{8/12}$ ,  $^1J_{\text{HH}} = 8.32$  Hz, 2H), 7.77 (d,  $\text{ArH}^{9/11}$ ,  $^1J_{\text{HH}} = 8.32$  Hz, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{C}} = 167.1$  (s,  $\text{C}=\text{O}$ ), 141.9 (s, CN), 141.7 (s,  $\text{C}^5$ ), 135.6 (s,  $\text{C}^{1/3}$ ), 135.3 (s,  $\text{C}^{4/6}$ ), 133.4 (s,  $\text{C}^2$ ), 133.3 (s,  $\text{C}^{8/12}$ ), 128.1 (s,  $\text{C}^{9/11}$ ), 118.2 (s,  $\text{C}^7$ ), 113.4 (s,  $\text{C}^{10}$ ).

**Synthesis of m-{(-C(O)-C<sub>6</sub>H<sub>4</sub>I-(C(O)PMe)}<sub>2</sub> (3a).** A diethyl ether solution of 5-Iodoisophthaloyl chloride (1 g, 3 mmol) was cooled via dry ice/IMS ( $-78^\circ\text{C}$ ) and MeP(SiMe<sub>3</sub>)<sub>2</sub> (0.7  $\text{cm}^3$ , 3 mmol) was added. During addition the solution assumes a purple coloration, after stirring at  $-78^\circ\text{C}$  for 30 mins the mixture was allowed to warm to ambient temperature and stirred for a further 16 h, whereupon the precipitate was collected by filtration, washed with diethyl ether and concentrated in vacuo. The product was extracted into toluene and dried in vacuo, resulting in 0.169 g of an orange-yellow solid in 18.5 % yield.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta_{\text{H}} = 9.43$  (br t,  $\text{ArH}^2$ , 1H), 7.87 (d,  $\text{ArH}^{4/6}$ ,  $^2J_{\text{HH}} = 1.41$  Hz, 2H), 1.61 (d, P-CH<sub>3</sub>,  $^2J_{\text{HP}} = 3$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ )<sup>29</sup>  $\delta_{\text{C}} = 205.4$  (d, C(O),  $^1J_{\text{CP}} = 46.5$  Hz), 139.9 (m,  $\text{Ar}^{4/6}$ ), 139.1 (d,  $\text{C}^{1/3}$ ,  $^2J_{\text{CP}} = 38$  Hz), 132.8 (t,  $\text{C}^2$ ,  $^3J_{\text{CP}} = 13.5$  Hz), 1.88 (d, CH<sub>3</sub>,  $^1J_{\text{CP}} = 4.5$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta_{\text{P}} = 36.3$  (s).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta_{\text{P}} = 36.1$  (s). IR  $\nu_{\text{CO}}$  1640 (br)  $\text{cm}^{-1}$ . HRMS (m/z): Calcd for  $\text{C}_{18}\text{H}_{12}\text{O}_4\text{P}_2\text{I}_2$  607.8300 ([M]<sup>+</sup>). Found 607.8306 ([M]<sup>+</sup>).

**Synthesis of m-{(-C(O)-C<sub>7</sub>H<sub>6</sub>-(C(O)PMe)}<sub>2</sub> (3b).** A diethyl ether solution of 5-methylisophthaloyl chloride (0.487 g, 2.25 mmol) was added, slowly, to a pre-cooled (dry ice/IMS;  $-78^\circ\text{C}$ ) ethereal solution of MeP(SiMe<sub>3</sub>)<sub>2</sub> (0.432 g, 2.25 mmol). During addition the solution assumes a yellow coloration. After stirring at  $-78^\circ\text{C}$  for 30 mins the mixture was allowed to warm to ambient temperature and stir for a further 16 h, whereupon the precipitate was collected by filtration, washed with diethyl ether (3 x 5  $\text{cm}^3$ ), hexanes (3 x 5  $\text{cm}^3$ ), Et<sub>2</sub>O again (3 x 5  $\text{cm}^3$ ) and dried in vacuo. Resulting in 94 mg of yellow solid in 22 % yield.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta_{\text{H}} = 9.34$  (br,  $\text{ArH}^2$ , 1H), 7.33 (br,  $\text{ArH}^{4/6}$ , 2H), 2.23 (s, Ar-CH<sub>3</sub>, 3H), 1.58 (d, P-CH<sub>3</sub>,  $^2J_{\text{HP}} = 2.7$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{C}} = 207.3$  (d, C(O),  $^1J_{\text{CP}} = 45.8$  Hz), 141.5 (br t,  $\text{C}^2$ ) 138.0 (d,  $\text{C}^{1/3}$ ,  $^2J_{\text{CP}} = 37.3$  Hz), 131.8 (s,  $\text{C}^5$ ), 131.6 (dd,  $\text{C}^{4/6}$ ,  $^3J_{\text{CP}} = 1.7$  Hz), 21.3 (s, Ar-CH<sub>3</sub>), 1.9 (d, P-CH<sub>3</sub>,  $^1J_{\text{CP}} = 4.2$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta_{\text{P}} = 34.2$  (s).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta_{\text{P}} = 32.3$  (s). IR  $\nu_{\text{CO}}$  1653  $\text{cm}^{-1}$ . HRMS (m/z): Calcd for  $\text{C}_{20}\text{H}_{18}\text{O}_4\text{P}_2$  384.0680 ([M]<sup>+</sup>). Found 384.0691 ([M]<sup>+</sup>).

**Synthesis of m-{(-C(O)-C<sub>10</sub>H<sub>12</sub>-(C(O)PMe)}<sub>2</sub> (3c).** To a precooled (Dry ice/IMS;  $-78^\circ\text{C}$ ) ethereal solution (5  $\text{cm}^3$ ) of MeP(SiMe<sub>3</sub>)<sub>2</sub> (0.254 g, 1.32 mmol) was added 5-tertbutyl isophthaloyl chloride (0.342 g, 1.32 mmol) dropwise over 5 minutes in ether (5  $\text{cm}^3$ ), resulting in yellow coloration of solution. After stirring for 30 minutes at  $-78^\circ\text{C}$  the mixture was allowed to warm to ambient temperature and stir for a further 16 hours, whereupon the precipitate was collected by filtration, washed with diethyl ether (2 x 5  $\text{cm}^3$ ) and dried in vacuo, affording 65 mg of an intense yellow solid in 21 % yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{H}} = 9.27$  (br m,  $\text{ArH}^2$ , 2H), 7.50 (d,  $\text{ArH}^{4/6}$ ,  $^1J_{\text{HH}} = 1.4$  Hz, 4H), 1.65 (d, CH<sub>3</sub>,  $^2J_{\text{PH}} = 2.7$  Hz, 6H), 1.1 (s, tBu (CH<sub>3</sub>)<sub>3</sub>, 18H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{C}} = 207.2$  (d, C(O),  $^1J_{\text{CP}} = 46$  Hz), 154.1 (br t,  $\text{C}^2$ ,  $^3J_{\text{CP}} = 1.7$  Hz), 137.5 (d,  $\text{C}^{1/3}$ ,  $^2J_{\text{CP}} = 37.6$  Hz), 131.2 (t,  $\text{C}^2$ ,  $^3J_{\text{CP}} = 13.5$  Hz), 127.5 (dd,  $\text{C}^{4/6}$ ,  $^3J_{\text{CP}} = 1.7$  Hz), 35.2 (s, C(CH<sub>3</sub>)<sub>3</sub>), 30.9 (s, C(CH<sub>3</sub>)<sub>3</sub>), 1.6 (d, CH<sub>3</sub>,  $^1J_{\text{CP}} = 3.9$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{P}} = 36.1$  (s).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta_{\text{P}} = 34.5$  (s). IR  $\nu_{\text{CO}}$  1657, 1641  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{26}\text{H}_{30}\text{O}_4\text{P}_2$ : C, 66.64; H, 6.46. Found: C, 66.54; H, 6.52.

**Synthesis of m-{(-C(O)-C<sub>12</sub>H<sub>8</sub>-(C(O)PMe)}<sub>2</sub> (3d).** A diethyl ether solution of 5-phenylisophthaloyl chloride (0.32 g, 1.1 mmol) was added, slowly, to a pre-cooled (Dry ice/IMS;  $-78^\circ\text{C}$ ) ethereal solution of MeP(SiMe<sub>3</sub>)<sub>2</sub> (0.22 g, 1.1 mmol). During addition the solution assumes a yellow coloration. After stirring at  $-78^\circ\text{C}$  for 30 mins the mixture was allowed to warm to RT and stirred for a further 12 h, whereupon the precipitate was collected by filtration, washed with diethyl ether and dried in vacuo, resulting in 77 mg of a yellow solid in 26 % yield.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta_{\text{H}} = 9.46$  (s,  $\text{ArH}^2$ , 1H), 7.71 (s,  $\text{ArH}^{4/6}$ , 2H), 7.34 (t, Ph, 5H), 1.66 (d, P-CH<sub>3</sub>,  $^2J_{\text{HP}} = 2.3$  Hz, 3H).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta_{\text{H}} = 9.21$  (br,  $\text{ArH}^2$ , 1H), 7.57 (d,  $\text{ArH}^{4/6}$ ,  $^2J_{\text{HH}} = 1.1$  Hz, 2H), 6.94 (t,  $\text{ArH}^{10}$ ,  $^1J_{\text{HH}} = 7.5$  Hz, 1H), 6.87 (t,  $\text{ArH}^{9/11}$ ,  $^1J_{\text{HH}} = 7.5$  Hz, 2H), 6.72 (d, aromatic  $\text{ArH}^{8/12}$ ,  $^1J_{\text{HH}} = 7.53$  Hz, 2H), 1.67 (d, CH<sub>3</sub>,  $^2J_{\text{HP}} = 2.9$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta_{\text{C}} = 207.4$  (d, C(O),  $^1J_{\text{CP}} = 45.8$  Hz), 144.3 (s, C<sub>10</sub>), 138.83 (d,  $\text{C}^{1/3}$ ,  $^2J_{\text{CP}} = 37.2$  Hz), 138.8 (s,  $\text{C}^7$ ), 132.6 (t,  $\text{C}^2$ ,  $^3J_{\text{CP}} = 12.6$  Hz), 129.5 (s,  $\text{C}^{8/12}$ ), 129.4 (s,  $\text{C}^{4/6}$ ), 129.1 (s,  $\text{C}^5$ ), 127.6 (s,  $\text{C}^{9/11}$ ), 1.9 (d, P-CH<sub>3</sub>,  $^1J_{\text{CP}} = 4.7$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta_{\text{P}} = 36.16$  (s).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta_{\text{P}} = 35.7$  (s). IR  $\nu_{\text{CO}}$  1658, 1639  $\text{cm}^{-1}$ . HRMS (m/z): Calcd for  $\text{C}_{30}\text{H}_{22}\text{O}_4\text{P}_2$  508.0993 ([M]<sup>+</sup>). Found 508.0996 ([M]<sup>+</sup>).

**Synthesis of m-{(-C(O)-C<sub>13</sub>H<sub>7</sub>N-(C(O)PMe)}<sub>2</sub> (3e)** To a cooled (Dry ice/IMS;  $-78^\circ\text{C}$ ) solution of 5-(4-cyanophenyl)isophthaloyl chloride (0.316 g, 1.04 mmol) in Et<sub>2</sub>O (5  $\text{cm}^3$ ) was added MeP(SiMe<sub>3</sub>)<sub>2</sub> (1.04 g, 1.04 mmol) resulting in an orange coloration. After stirring for 30 minutes at this temperature, the mixture was allowed to warm to ambient temperature and stir for a further 16 hours. At this point the reaction had only proceeded halfway warranting the addition of another equivalent of MeP(SiMe<sub>3</sub>)<sub>2</sub> (1.04 g, 1.04 mmol) and stirred for a further 16 hours, whereupon the orange precipitate was collected by filtration, washed with Et<sub>2</sub>O (3 x 10  $\text{cm}^3$ ) and dried in vacuo. Yield: 69 mg, 24 %.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta_{\text{H}} = 9.29$  (br,  $\text{ArH}^2$ , 1H), 7.43 (d,  $\text{ArH}^{4/6}$ ,  $^2J_{\text{HH}} = 1.5$  Hz, 2H), 6.82 (d,  $\text{ArH}^{8/12}$ ,  $^1J_{\text{HH}} = 8.5$  Hz, 2H), 6.33 (d,  $\text{ArH}^{9/11}$ ,  $^1J_{\text{HH}} = 8.5$  Hz, 2H), 1.66 (d, CH<sub>3</sub>,  $^2J_{\text{HP}} = 3.1$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta_{\text{C}} = 205.9$  (d, C(O),  $^1J_{\text{CP}} = 46.4$  Hz), 141.8 (s, CN), 141.4 (s,  $\text{C}^7$ ), 138.5 (d,  $\text{C}^{1/3}$ ,  $^2J_{\text{CP}} = 37.8$  Hz), 133.4 (t,  $\text{C}^2$ ,  $^3J_{\text{CP}} = 13.3$  Hz), 132.5 (s,  $\text{C}^{8/12}$ ), 129.1 (dd,  $\text{C}^{4/6}$ ,  $^3J_{\text{CP}} = 1.9$  Hz), 127.3 (s,  $\text{C}^{9/11}$ ), 118.2 (s,  $\text{C}^5$ ), 112.9 (s,  $\text{C}^{10}$ ), 1.8 (d, CH<sub>3</sub>,  $^1J_{\text{CP}} = 4.63$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta_{\text{P}} = 35.2$  (s). IR  $\nu_{\text{CO}}$  1648 (br)  $\text{cm}^{-1}$   $\nu_{\text{CN}}$  2227  $\text{cm}^{-1}$ . HRMS (m/z): Calcd for  $\text{C}_{32}\text{H}_{20}\text{N}_2\text{O}_4\text{P}_2$  558.0898 ([M]<sup>+</sup>). Found 558.0906 ([M]<sup>+</sup>).

**Synthesis of m-{(-C(O)-C<sub>8</sub>NH<sub>4</sub>-(C(O)PMe)}<sub>2</sub> (4).** A diethyl ether solution of 2,6-pyridinedicarbonyl dichloride (0.312 g, 1.5 mmol) was added, slowly, to a pre-cooled (Dry ice/IMS;  $-78^\circ\text{C}$ ) ethereal solution of MeP(SiMe<sub>3</sub>)<sub>2</sub> (0.294 g, 1.5 mmol). During addition the solution assumes a green-yellow coloration. After stirring at  $-78^\circ\text{C}$  for 30 mins the mixture was allowed to warm to ambient temperature and stirred for a further 16 h, whereupon the precipitate was collected by filtration, washed with diethyl ether and dried in vacuo, resulting in 0.161 g of a green-yellow solid in 60 % yield.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta_{\text{H}} = 7.2$  (d,  $\text{ArH}^{4/6}$ ,  $^2J_{\text{HH}} = 7.8$  Hz, 4H), 6.58 (t,  $\text{ArH}^5$ ,  $^2J_{\text{HH}} = 7.8$  Hz, 2H), 1.63 (d, CH<sub>3</sub>,  $^2J_{\text{PH}} = 6.2$  Hz, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta_{\text{C}} = 209.1$  (d, C(O),  $^1J_{\text{CP}} = 50.86$  Hz), 152.9 (d,  $\text{C}^{1/3}$ ,  $^2J_{\text{CP}} = 33.1$  Hz), 138.4 (s,  $\text{C}^{4/6}$ ), 124.7 (br t,  $\text{C}^5$ ,  $^3J_{\text{CP}} = 1.7$  Hz), 3.65 (dd, CH<sub>3</sub>,  $^1J_{\text{CP}} = 7.2$  Hz).

$^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta_{\text{P}} = 30.1$  (s). IR  $\nu_{\text{CO}}$  1656, 1640  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_4\text{P}_2$ : C, 53.63; H, 3.38; N, 7.82. Found: C, 52.89; H, 3.34; N, 7.80.<sup>30</sup>

**Synthesis of m-{C(O)-C<sub>6</sub>H<sub>4</sub>(C(O)PPh)}<sub>2</sub> (5).** Isophthaloyl chloride (0.5 g, 2.46 mmol) was dissolved in diethyl ether (6  $\text{cm}^3$ ) and slowly added dropwise to a pre-cooled (dry ice/IMS;  $-78^\circ\text{C}$ ) ethereal solution (10  $\text{cm}^3$ ) of  $\text{PhP}(\text{SiMe}_3)_2$  (0.627 g, 2.46 mmol) over 5 minutes yielding a yellow color change. The yellow solution was stirred for 30 minutes at  $-78^\circ\text{C}$ , then allowed to warm to RT and stir for 16 hours leading to a yellow precipitate which was filtered, washed with diethyl ether (3 x 5  $\text{cm}^3$ ) and dried in vacuo, initially yielding 0.181 g of yellow powder. The solid was dissolved in the minimum amount of DCM and layered with pentane resulting in 0.102 g of matt yellow solid isolated in 17% yield.<sup>23</sup>  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta_{\text{H}} = 8.50$  (br,  $\text{ArH}^2$ , 1H), 8.21 (br,  $\text{ArH}^5$ , 1H), 8.03 (br,  $\text{ArH}^{4/6}$ , 2H), 7.33 (br,  $\text{PhH}^{\text{P}} + \text{PhH}^{\text{m}}$ , 3H),<sup>31</sup> 7.48 (br,  $\text{PhH}^{\text{o}}$ , 2H).<sup>31</sup>  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):<sup>32</sup>  $\delta_{\text{C}} = 208.5$  (d, C(O),  $^1J_{\text{CP}} = 35.1$  Hz), 140.3 (d,  $^1J_{\text{CP}} = 34$  Hz, P-Ph<sup>1</sup>), 137.9 (d,  $^2J_{\text{CP}} = 19.5$  Hz, P-Ph<sup>o</sup>), 133.4 (s,  $\text{Ar}^{4/6}$ ), 129.7 (d,  $^2J_{\text{CP}} = 6.8$  Hz, P-Ph<sup>m</sup>), 129.3 (m,  $\text{Ar}^2$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta_{\text{P}} = 30.5$  (s).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta_{\text{P}} = 32.2$  (s). IR  $\nu_{\text{CO}}$  1639 (w)  $\text{cm}^{-1}$ . HRMS (m/z): Calcd for  $\text{C}_{28}\text{H}_{18}\text{O}_4\text{P}_2$  480.0680 ([M]<sup>+</sup>). Found 480.0699 ([M]<sup>+</sup>).

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Plots of  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  and 2D ( $^1\text{H}$ - $^{13}\text{C}$  HSQC, HMBC) NMR spectra and HRMS for all compounds. UV-vis spectra, calculated excited states and spectra and cyclic voltammograms. X-ray collection / refinement data and Ortep plots for 3a-5. Computational methods (PDF)

DFT optimized geometries (coordinates and energies) (XYZ)

### Accession codes

CCDC 2009986-2009992 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/dta\\_request/cif](http://www.ccdc.cam.ac.uk/dta_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ; fax +44 1223 336033.

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### Notes

The authors declare no competing financial interest.

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(22) The cyclophanes all exhibit partial solubility in Et<sub>2</sub>O and most hydrocarbon solvents, albeit reduced in comparison to the impurities and by-products generated. Nonetheless, purification (washing or recrystallization) incurs appreciable losses, accounting for the low isolated yields reported. The sensitivity of the compounds has precluded, thus far, the use of chromatography as a more efficient means of purification.

(23) Both <sup>1</sup>H and <sup>13</sup>C NMR spectra for this compound show appreciable broadening and poor resolution, possibly suggestive of a dynamic process. Additionally, the 2D spectra (HSQC, HMBC) show limited correlations implying enhanced relaxing precluding the evolution of CH coupling. Cooling the samples through to -80 °C feels to arrest any dynamism, though does show a marginal resolution enhancement. We can thus not convincingly demonstrate bulk purity, though data provide confidence that **5** is the sole phosphorus containing component and amounts to the bulk product.

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(25) As is often observed, the spectroscopic envelopes computed with the B3LYP functional do not quantitatively reproduce the intensity data observed experimentally, though do offer a qualitative comparison. This is most prominently apparent for **1**, **3b** and **3c**, for which absorbance energies are, nonetheless, reasonably reproduced. In order to confirm the validity of these data in assisting our assignments the spectrum for **1** was also computed using the CAM-B3LYP and M062x methods (SI figures S76-77). These do reproduce more accurately the overall shape and intensity of the experimental spectrum, though illustrate precisely the same features (absorbance energies) with negligible variation in energies or indeed originating transitions. As such we are confident that our calculations at the B3LYP level of theory are adequate in aiding general assignment of the originating transitions.

(26) We note that the highest energy feature in each UV-vis spectrum (ca 225 nm) appears unusually sharp. We have recorded the spectra across several concentrations (10<sup>-3</sup>, 10<sup>-4</sup>, 10<sup>-5</sup>, 10<sup>-6</sup> M) and different path lengths (1 cm, 0.5 cm, see SI) to equivalent effect; we have also determined there is no solvent effect at play by recording some representative data in benzene. Indeed, the resulting spectra

were fully comparable. We have additionally recorded representative data on three separate instruments, which each reproduce the same general features (SI figure S106); we note that those obtained on the Varian instrument appear less angular and more akin to a classic spectrum, but nonetheless demonstrate the comparable feature around 225 nm (marginally shifted between instruments). The wavelength of this unusual feature varies between the compounds and this is also reflected in the computed data, which suggest absorbance in this region to be associated with a single, dominant transition, giving rise to a relatively sharp band. We thus reasonably conclude that this constitutes, or is at the very least coincident with, a real feature of the absorption spectra as presented.

(27) The LUMO energies are estimated using the equation  $E_{LUMO} = -(4.8 + {}^1E_{1,2})$  using the half-wave potential for the first pseudoreversible reductive event, relative to the Fc/Fc<sup>+</sup> couple, as widely utilized in related systems.<sup>8</sup>

(28) For the irreversible event associated with **3a** the LUMO energy is estimated from the same equation<sup>24</sup> using  $E_{pc}$  for the single reductive feature in place of the half-wave potential.

(29) The carbon resonance for the 5-position bearing iodine cannot be confidently assigned. The HMBC spectrum appears to show a correlation from the adjacent protons to 153 ppm, however, no signal is resolved in the 1D <sup>13</sup>C{<sup>1</sup>H} spectrum, presumably due to it being a heavily relaxed quaternary center. As such, this is not assigned.

(30) The metacyclophanes are all sensitive to air and moisture and thus typically resistant to the acquisition of acceptable EA data. In the case of **4**, the compound is also prone to fragmentation (as noted in Balakrishna's work and our own efforts to effect its coordination to metals) which has precluded acquisition of HRMS as an alternative indicator of purity / composition. The combination of spectroscopic and crystallographic data presented offers some (albeit qualified) mitigation in this regard, but certainly demonstrates adequate purity to ensure the validity of the subsequent electronic studies.

(31) The resonances at 7.48 and 7.33 ppm are deconvoluted using line fitting. Recourse to the HSQC spectrum allows resolution of two distinct resonances within the envelope at 7.33, viz.: 7.32 and 7.36 ppm, corresponding respectively to the meta and para protons of the P-phenyl as demonstrated by coupling magnitude in the carbon spectrum.

(32) Remaining carbon centers are not convincingly resolved or assignable from the 2D spectra, which exhibit limited correlations, presumably resulting from enhanced relaxation effects precluding evolution of the CH coupling.

